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GA-6472

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ON MATERIALS OF THERMIONIC INTEREST**

by

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FACILITY FORM 602

N66 29388	(THRU)
(ACCESSION NUMBER)	1
15	(CODE)
(PAGES)	17
CR-64468	(CATEGORY)
(NASA CR OR TMX OR AD NUMBER)	

LED PRICE \$ _____

OSTI PRICE(S) \$ _____

June 28, 1968

Hard copy (HC) 1.00

Microfiche (MF) 150

CASE FILE COPY

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This is a preprint of a paper to be presented at the
International Conference on Thermionic Electrical Power
Generation in London, September 20-24, 1965.

* This work was supported by the National Aeronautics
and Space Administration under Contract NAS3-6471.

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ABSTRACT. Studies have been made on the diffusion between a number of uranium-containing materials and various refractory metals and alloys in the temperature range 1400-2000°C. Results are presented on the nature of interaction at the interfaces of these diffusion couples and the effect of composition, stoichiometry and temperature on the stability of vacuum electron emission properties of tungsten clad UO_2 and UC-ZrC.

INTRODUCTION. As a part of a program aimed at the improvement of our understandings of the mass transport properties of high temperature materials of thermionic interest, studies have been made on the diffusion between a number of uranium-containing materials (UC, UC-ZrC, UC_2 and UO_2) and various refractory metals and alloys (W, Mo, Ta, Nb, Ir, Re, W-25 Re, W-15 Mo and W-2 Mo) in the temperature range 1400-2000°C. These studies were directed toward the following two objectives: (i) to establish the nature of any gross interaction occurring at the interface, and (ii) to determine the stability of the vacuum electron emission characteristics of refractory metal clad uranium compounds as a function of composition, stoichiometry and temperature.

GROSS DIFFUSION STUDIES. The experimental techniques used in the gross diffusion studies have been described previously⁽¹⁾ and are therefore reviewed only briefly as follows. The high purity (> 99.9% pure) refractory metals and alloys were procured from commercial sources and the uranium compounds were prepared in our laboratory by cold-pressing and sintering of carbide and oxide powders of controlled composition and stoichiometry. All the samples used were in the form of cylindrical pellets, 0.250 inch in diameter and 0.187 inch in height, with their top and bottom surfaces ground parallel and polished metallographically. A number of these cylindrical pellets were stacked in a pre-determined sequence in a tantalum diffusion die, containing a screw cap and lined with tungsten foils to provide the diffusion couples of interest. The height of the stack was adjusted with tungsten spacers so that the surfaces of the samples could be pressed into good contact when the screw cap was tightened with a torque of 10 lb-in. Diffusion-anneal was carried out in vacuum resistance furnace provided with temperature control and monitoring devices to enable the test temperatures to be controlled to better than $\pm 10^\circ\text{C}$. During the test, the temperature of the samples was measured with a calibrated micro-optical pyrometer, sighting into a hohlraum drilled into the side of the die. After each test, the samples were examined both metallographically and by electron microprobe techniques to determine the structures and the composition distributions near the interface of each couple.

*Work sponsored by the U. S. National Aeronautics and Space Administration under Contract Number NAS 3-6471.

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Table 1 summarizes the results obtained to date, including those described in previous publications⁽¹⁾⁽²⁾⁽³⁾ from this laboratory. Some of the more significant results regarding UC, UC-ZrC and UO_2 are described as follows:

UC and UC-ZrC. Tungsten does not react with UC and UC-ZrC at 1800° . At 2000°C in 1000 hours, with three thermal cycles to room temperatures, tungsten reacts with 80 UC-20 ZrC (~ 3 mole % carbon-rich), 50 UC-50ZrC (stoichiometric) and 30 UC-70 ZrC (stoichiometric) to form tungsten and uranium-rich phases in the carbide, although no uranium and zirconium are detected (within 0.1%) in the tungsten. Figure 1(a) and (b) illustrate the electron microprobe scan of the interface of the W-(30UC-70ZrC) couple after such a diffusion test.

Rhenium is stable for at least 100 hours toward hyperstoichiometric UC ($\text{U}_{.484}\text{C}_{.516}$) at 1800°C , but reacts with the UC-ZrC studied even at 1600°C or 1400°C . Figures 2(a)--(c) shows the electron microprobe scan of a Re-(30UC-70 ZrC) interface reacted at 1800°C for 50 hours. The reaction zone contains Re and U but very little, if any, Zr; and Re is detected in the carbide beyond the reaction zone. The reaction between Re and stoichiometric UC at 1800°C is similar to that between Re and 30UC-70ZrC at 1800°C .

Similar to rhenium the tungsten - 25 rhenium alloy is stable for at least 100 hours toward hyperstoichiometric UC ($\text{U}_{.484}\text{C}_{.516}$) at 1800°C , but reacts with stoichiometric UC and the UC-ZrC studied even at 1600°C or 1400°C . Figures 3(a) and (b) show the microstructure and the electron microprobe scan of a W 25 Re-(30 UC-70 ZrC) interface reacted at 1800°C for 50 hours. The mode of interaction consists of grain boundary penetration of uranium from the carbide into the alloy, although the mechanism by which the grain boundary penetration occurs is not clear.

Of the other cases studied, only the Mo-(10 UC-90 ZrC) combination is stable at 1800°C . All the others react at 1800°C or even at 1400°C .

UO_2 . No gross reaction was observed between UO_2 and all the refractory metals studied at 1800°C for 100 hours except in the case of Ir which reacts with UO_2 at 1600°C to form an interfacial layer containing both U and Ir (in approximately 1:3 ratio). At 2000°C in 1000 hours, with three thermal cycles to room temperature, no gross reaction was observed between UO_2 and W; however, uranium-rich precipitates were observed along some tungsten grain boundaries near the UO_2 - W interface (see Figure 4). Similar studies made on W 25 Re- UO_2 and Re- UO_2 couples showed no deep penetration of uranium into the metal but uranium-rich phase was detected in the W25 Re along the UO_2 -W25 Re interface in an irregular fashion to a maximum depth of 60 microns; and uranium-rich phase was also detected in Re along the UO_2 -Re interface in small local concentrations to a maximum depth of 100 microns. Uranium-rich phase was observed in the UO_2 in each case, as shown typically in Figure 5.

STABILITY OF VACUUM EMISSION CHARACTERISTICS OF TUNGSTEN CLAD UC, UC-ZrC AND UO_2 . It is generally recognized that the presence of a fraction of a monolayer of impurities on the surface of an electron emitter may cause serious changes in its emission characteristics. Therefore even though tungsten does not exhibit gross interaction with UC, UC-ZrC and UO_2 at 1800°C , it is not certain whether trace amounts of the components of the carbide or the oxide could diffuse to the tungsten surface and, if the arrival rate is higher than the vaporization rate, could accumulate there to change the electron emission characteristics of the tungsten surface. To resolve this problem, UC, UC-ZrC and UO_2 were clad with tungsten

formed by the reduction of WF_6 with H_2 and the tungsten clad samples were heated in vacuum (10^{-7} - 10^{-8} torr) by electron bombardment and the current voltage relationship between the tungsten surface and a water-cooled collector-guard ring assembly was followed for periods of $(2)(4)$ 1000--2000 hours, using the experimental arrangement described previously. For small emission currents a conventional D.C. power supply was used and the current-voltage relationship was read directly. For large emission currents, a pulsed D.C. power supply (20 pulses per second and 100 microsecond per pulse) was used to avoid the overheating of the collector surface and the current-voltage relationship was shown on an oscilloscope. A total of seventeen samples having tungsten clad thickness from 12 to 40 mils were studied at 1800°C to 2200°C . The results indicate that the composition and the stoichiometry of the uranium containing material, and the diffusion temperature are influential factors in determining the stability of the vacuum electron emission characteristics of the tungsten cladding, as outlined below.

1. Tungsten-clad $\text{UO}_{2.005}$ exhibited stable vacuum emission characteristics at 1800°C .

2. For tungsten clad UC-ZrC of high UC contents, e.g., 90 UC-10ZrC, carbon contents in excess of stoichiometric amounts are needed to maintain stable vacuum emission characteristics at 1800°C . The degree of excess carbon needed seems to increase with the increase of the UC content. For instance, the vacuum emission of tungsten clad $\text{UC}_{1.02}$, though slightly carbon-rich, still increased continuously with time at 1800°C (Figure 6), while for tungsten clad 50 UC-50 ZrC and 30 UC-70 ZrC stable vacuum emission characteristics can be maintained at 1800°C even if the carbon contents are stoichiometric. It is believed that a few mole percent of excess carbon in the carbide is sufficient to maintain the vacuum emission stability of tungsten clad UC-ZrC of high UC content, such as 90 UC-10ZrC, as shown by the results obtained on a tungsten clad $\text{U}_{0.88}\text{Zr}_{0.12}\text{C}_{1.03}$ sample and illustrated in Figure 7. It must be pointed out, however, that the excess carbon is needed not only for lowering the uranium activity and thus the driving force of uranium diffusion through the tungsten cladding, but also to satisfy the solubility of carbon in tungsten. Therefore, the higher are the UC content of the carbide and the tungsten to carbide ratio in the sample, the higher should be the carbon content in the carbide if the stability of the vacuum emission characteristics of the tungsten is to be maintained.

3. Studies made on the vacuum emission stability of tungsten clad UO_2 and UC-ZrC in 300-hour durations at temperatures successively higher than 1800°C demonstrate that tungsten clad $\text{UO}_{2.005}$ can maintain its vacuum emission stability even at 2200°C , while tungsten clad $\text{U}_{0.90}\text{Zr}_{0.10}\text{C}_{1.02}$ exhibits vacuum emission degradation at 2000°C (see Figure 8). Metallographic and electron microprobe examinations made on the tungsten clad $\text{UO}_{2.005}$ sample after the test show the presence of tungsten and uranium precipitates in the UO_2 and uranium-rich precipitates in the grain boundaries of the tungsten cladding. Similar studies made on the tungsten clad carbide sample reveal the presence of tungsten in the carbide but no uranium or zirconium (within 0.1%) in the tungsten. Although the maximum temperature at which vacuum emission stability can be maintained depends upon the thermal history of the sample as well as thermal cycling effects, the results seem to indicate that it is easier to maintain a clean tungsten surface at high temperatures when the tungsten is in contact with UO_2 than in contact with UC-ZrC. This is

presumably because the carbon atoms diffusing to the tungsten surface from carbide tend to stabilize the uranium atoms reaching there by similar diffusion processes and the presence of such an adsorbed uranium layer reduces the electron work function of the tungsten surface. On the other hand, the oxygen atoms derived from UO_2 may not be effective as a "uranium stabilizer" because of the high volatility of oxygen and uranium oxides.

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TABLE 1

COMPATIBILITY OF VARIOUS FUELS AND REFRACTORY METALS AS
DETERMINED BY CROSS-DIFFUSION EXPERIMENTS AT VARIOUS
EXPERIMENTAL TEMPERATURES FOR 50 HR TO 100 HR

THE EXPERIMENTAL TEMPERATURES ARE IN °C. SUITABLE COMBINATIONS
AT SPECIFIC EXPERIMENTAL TEMPERATURES ARE INDICATED BY ✓.
UNSUITABLE COMBINATIONS BY X, AND QUESTIONABLE COMBINATIONS
BY ?. PARENTHESES AROUND THE ✓, X, OR ? INDICATE A JUDGEMENT
BY DEDUCTION.

REFRACTORY METAL	UC				90 UC-10 ZrC				80 UC-20 ZrC				50 UC-50 ZrC				30 UC-70 ZrC				10 UC-90 ZrC				UC ₂				UO ₂				
	1400	1600	1800	2000	1400	1600	1800	2000	1400	1600	1800	2000	1400	1600	1800	2000	1400	1600	1800	2000	1400	1600	1800	2000	1400	1600	1800	2000	1400	1600	1800	2000	
	✓	(✓)	✓	X ^a	(✓)	(✓)	✓		(✓)	(✓)	✓	X ^a	(✓)	(✓)	✓	X ^a	(✓)	(✓)	✓	X ^a	(✓)	(✓)	✓	X ^b	(X)	(✓)	(✓)	✓	X ^c	(X)	✓	X ^c	(X)
TUNGSTEN		X ^d	X ^e	(X)			X ^e	(X)		X ^e	X ^e	(X)	X ^d	X ^e	X ^e	(X)	X ^d	X ^e	X ^e	(X)	(✓)	(✓)	✓	X ^b	(X)	(✓)	✓	X ^c	(X)	✓	X ^c	(X)	
MOLYBDENUM		X ^e	X ^e	(X)		X ^e	(X)	(X)		X ^e	(X)	(X)	X ^d	X ^b	(X)	(X)	X ^d	X ^b	(X)	(X)			X ^d	(X)	(✓)	✓	✓	✓	✓	X ^c	(X)		
NIOBIUM		X ^b	X ^e	(X)		X ^e	(X)			X ^d	(X)	(X)	X ^d	X ^b	(X)	(X)	X ^d	X ^b	(X)	(X)			X ^d	(X)	(✓)	✓	✓	✓	✓	✓	✓	✓	✓
TANTALUM			X ^e	(X)		X ^e	(X)			X ^d	(X)	(X)	X ^d	X ^b	(X)	(X)	X ^d	X ^b	(X)	(X)			X ^d	(X)	(✓)	✓	✓	✓	✓	✓	✓	✓	✓
IRIDIUM			X ^e	(X)						X ^g	(X)	(X)	X ^g	X ^g	(X)	(X)	X ^g	X ^g	X ^g	X ^d	(X)							X ^g	(X)	(X)			
RHENIUM	(✓)	✓	✓ ^h							X ^g	X ^g	(X)	X ^g	X ^g	(X)	(X)	X ^g	X ^g	X ^g	X ^g	(X)				(✓)	✓	✓ ^f	✓ ^f	✓ ^f	✓ ^f	✓ ^f	✓ ^f	✓ ^f
W - 25 Re		X ^c	✓ ^h							X ^c	X ^c	(X)	X ^c	X ^c	(X)	X ^c	X ^c	X ^c	X ^c	X ^c	(X)						(✓)	✓	✓ ^f	✓ ^f	✓ ^f	✓ ^f	✓ ^f
W - 15 Mo			X ^e	(X)																													
W - 2 Mo			X ^e	(X)																X ^e	(X)												

^aReaction of fuel with metal, with the formation of new phases in fuel.

^bExcessive carbide formation at interface and at grain boundaries of metal.

^cDiffusion of uranium through grain boundaries of metal.

^dRapid frontal diffusion of uranium and/or zirconium into metal.

^eLiquid phase formation.

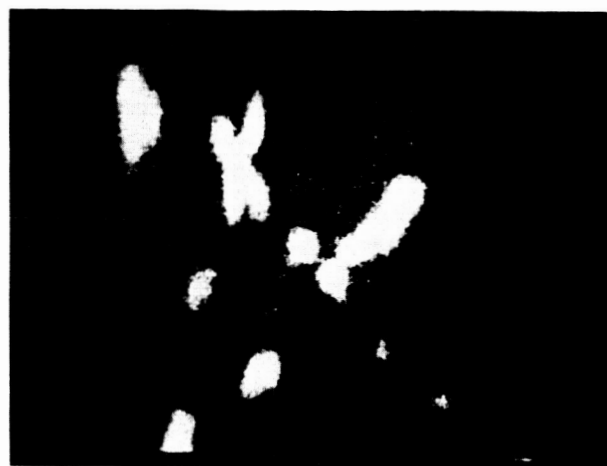
^fUranium diffusion into metal to a slight extent.

^gFormation of interfacial reaction zone.

^hCarbon-rich UC was used

NOTE: The following tests are of 1000 hr duration:

- (1) 80UC-20ZrC, 50UC-50ZrC and 30UC-70ZrC versus W at 2000°C
- (2) UO₂ versus W, Re and W 25Re at 2000°C
- (3) UO₂ versus Mo, Nb and Ta at 1600°C.

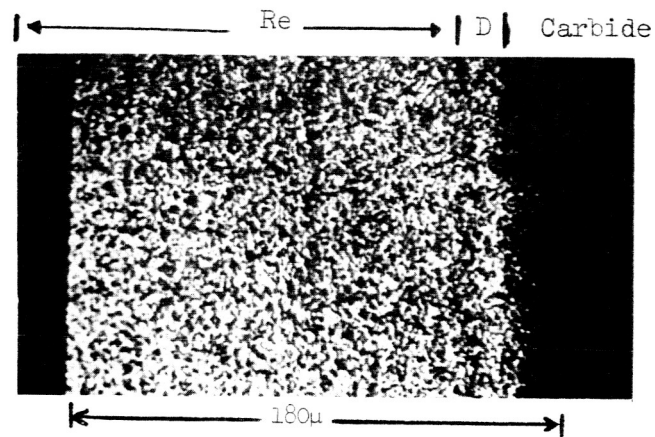


$\longleftrightarrow 90\mu$
 (a) W (L_{α}) 120μ from interface

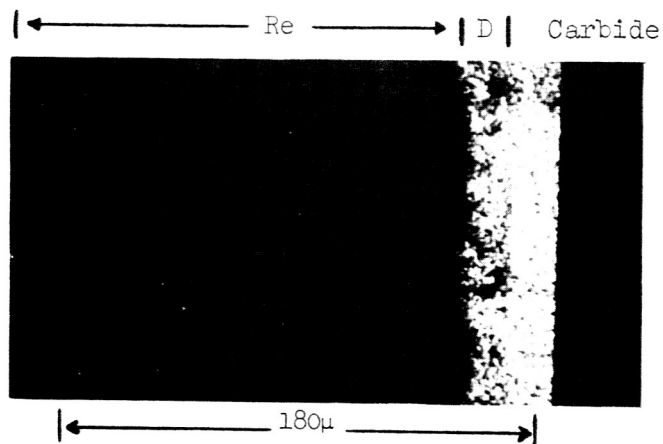


$\longleftrightarrow 90\mu$
 (b) U (M_{α}) 120μ from interface

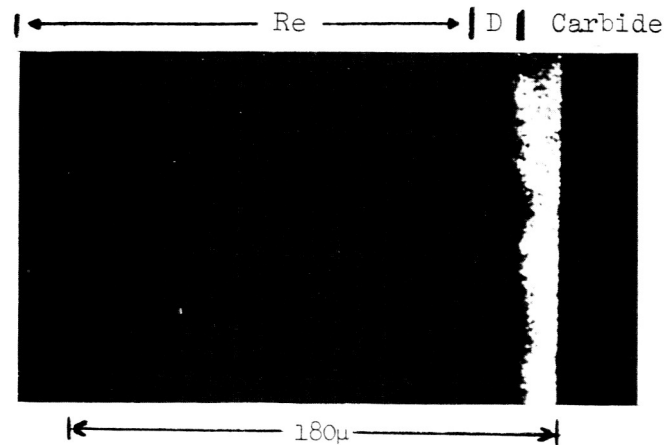
Fig. 1--Electron microprobe scan of tungsten-(30UC-70ZrC) interface after the couple was held at 2000°C for 1000 hr, showing tungsten and uranium-rich phases in the carbide.



(a) Re (L_{α}) scan reveals presence of Re in carbide beyond main diffusion zone D

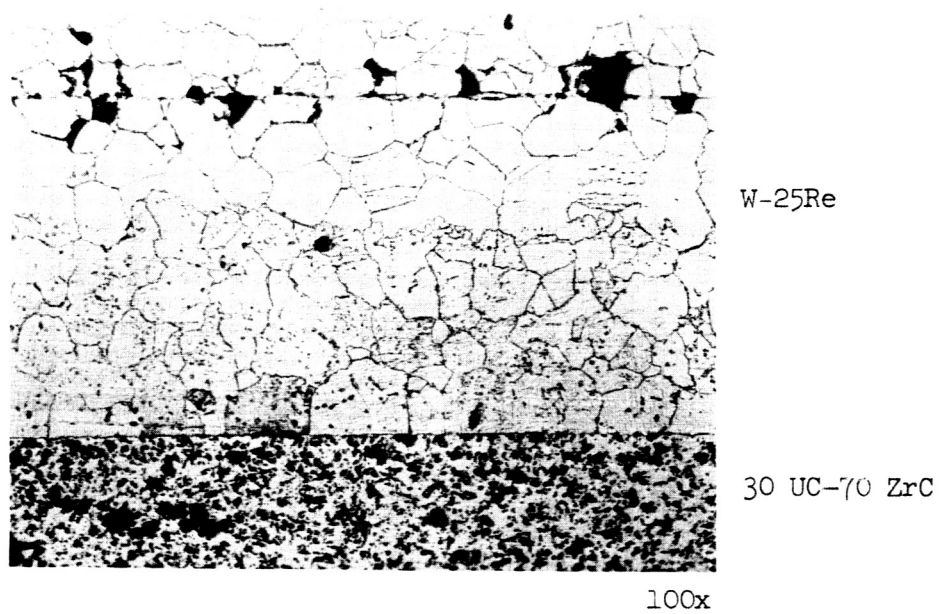


(b) U (M_{α}) scan reveals presence of uranium in main diffusion zone D

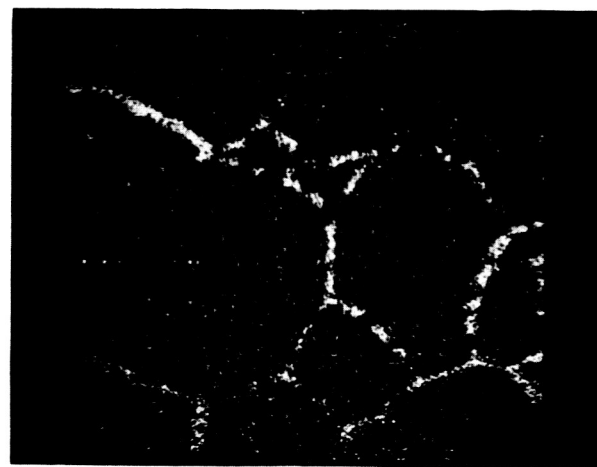


(c) Zr (L_{α}) scan reveals presence of very little, if any, Zr in main diffusion zone D

Fig. 2--Electron microprobe scan of rhenium-(30UC-70ZrC) interface after the couple was held at 1800°C for 50 hrs.



(a) Microstructure at interface



(b) U (M_{α}) scan in W25Re near interface

Fig. 3--W-25Re reaction with 30 UC-70 ZrC at 1800°C for 50 hr

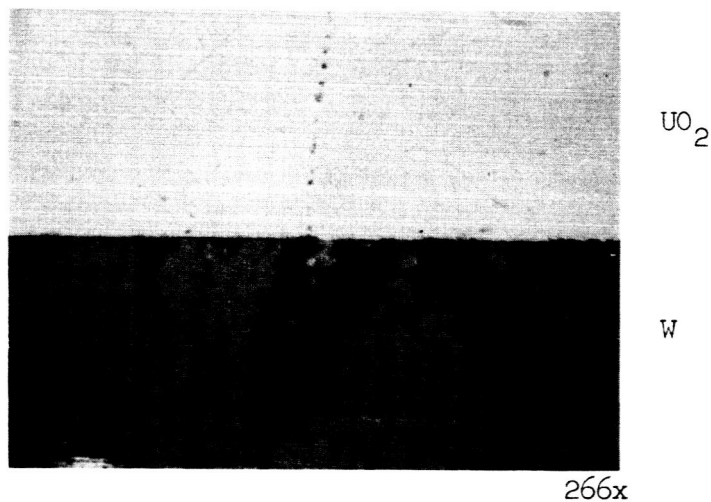


Fig. 4--Tungsten- UO_2 interface after 1000 hr at $2000^{\circ}C$, showing uranium-containing precipitate at grain boundary of tungsten

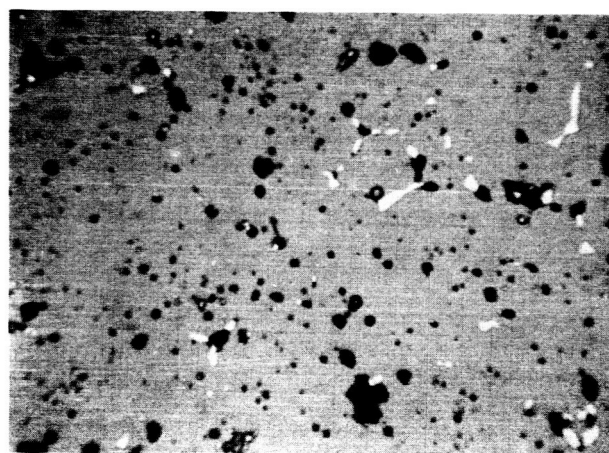
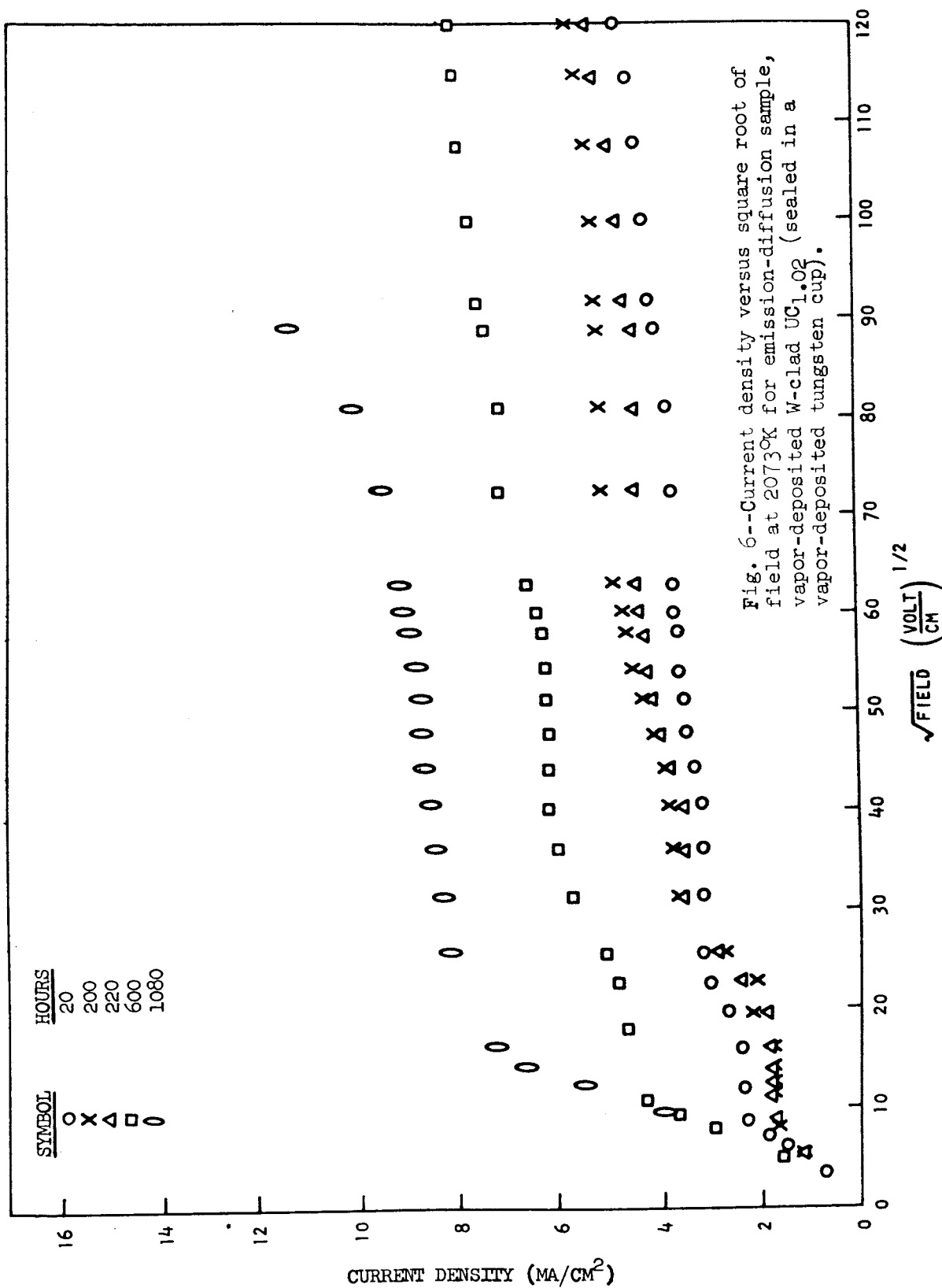


Fig. 5--Presence of uranium-rich phase in UO_2 after 1000 hr at 2000° in contact with W-25Re



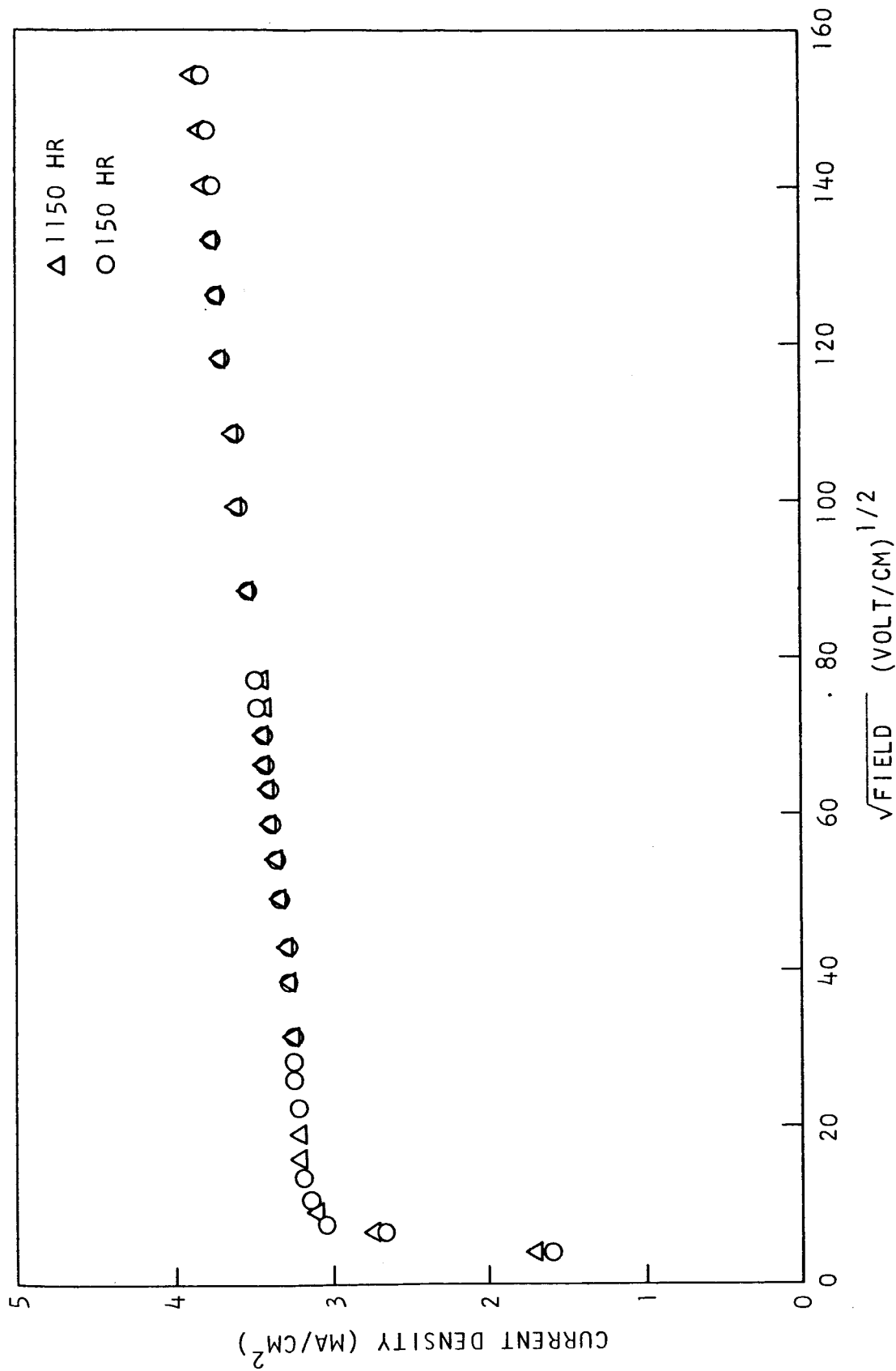


Fig. 7--Current density vs $(\text{field})^{1/2}$ plots for a tungsten clad $\text{U}_{0.88}\text{Zr}_{0.12}\text{C}_{1.03}$ sample after 150 and 1150 hours at 1800°C .

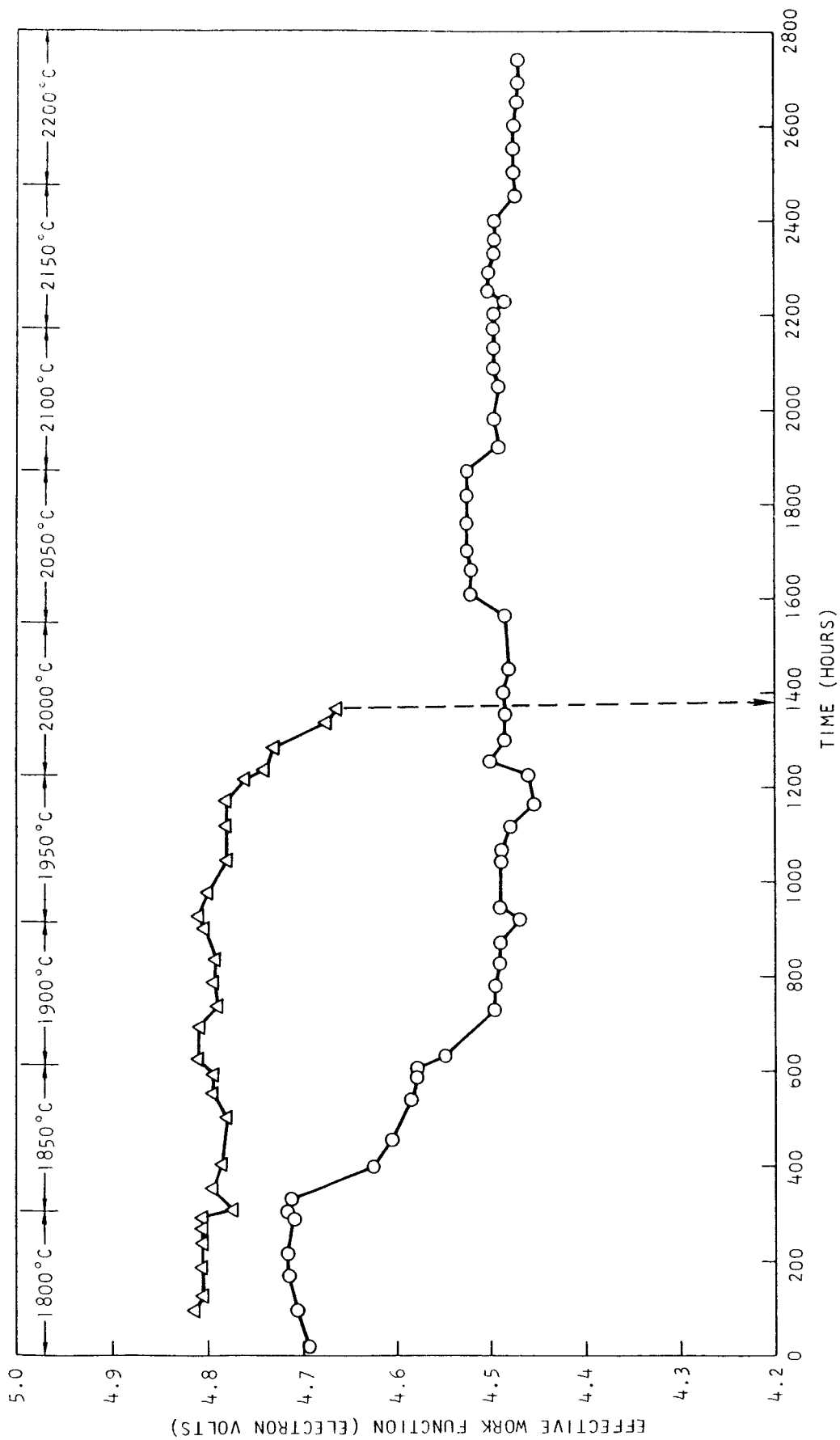


Fig. 8--Variation of effective work function with time and temperature for a tungsten clad $UO_{2.005}$ sample (represented by o) and a tungsten clad $U_{0.90}Zr_{0.10}C_{1.02}$ sample (represented by x).